

## PROBLEMS

1. (a)  $35^{\circ}\text{C}$ :  $254 \text{ mm Hg} \times \frac{308 \text{ K}}{330 \text{ K}} = 237 \text{ mm Hg}$        $45^{\circ}\text{C}$ :  $254 \text{ mm Hg} \times \frac{318 \text{ K}}{330 \text{ K}} = 245 \text{ mm Hg}$
- (b)  $35^{\circ}\text{C}$ :  $237 \text{ mm Hg} > \text{vp CH}_3\text{OH}$        $45^{\circ}\text{C}$ :  $245 \text{ mm Hg} < \text{vp CH}_3\text{OH}$
- (c)  $35^{\circ}\text{C}$ :  $203 \text{ mm Hg}$        $45^{\circ}\text{C}$ :  $245 \text{ mm Hg}$
- (d)  $35^{\circ}\text{C}$ : liquid, vapor       $45^{\circ}\text{C}$ : vapor

3. (a)  $n = \frac{(0.300/760 \text{ atm})(1.000 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(298 \text{ K})} = 1.61 \times 10^{-5} \text{ mol}$

mass =  $(1.61 \times 10^{-5} \text{ mol})(128.2 \text{ g/mol}) = 0.00207 \text{ g} = 2.07 \text{ mg}$

(b) Assume all the naphthalene sublimes.

$$P_{\text{calc}} = \frac{(7.00 \times 10^{-4} \text{ g}) \times (1 \text{ mol}/128.2 \text{ g}) \times (0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}) \times (298 \text{ K})}{1.000 \text{ L}} = 1.34 \times 10^{-4} \text{ atm}$$

$$= 0.102 \text{ mm Hg}$$

$\text{VP} > P_{\text{calc}}$ ; assumption is correct;  $P$  in the flask is  $0.102 \text{ mm Hg}$ . The flask contains only vapor.

(c) Assume all the naphthalene sublimes.

$$P_{\text{calc}} = \frac{(4.00 \times 10^{-3} \text{ g}) \times (1 \text{ mol}/128.2 \text{ g}) \times (0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}) \times (298 \text{ K})}{1.000 \text{ L}} = 7.63 \times 10^{-4} \text{ atm}$$

$$= 0.580 \text{ mm Hg}$$

$\text{VP} < P_{\text{calc}}$ ; assumption is wrong;  $P$  in the flask is  $0.300 \text{ mm Hg}$ . The flask contains solid and vapor.

5. (a)  $n = \frac{(228/760 \text{ atm}) \times (2.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}) \times (298 \text{ K})} = 0.0245 \text{ mol}$ ;      mass =  $0.0245 \text{ mol} \times 159.8 \text{ g/mol} = 3.92 \text{ g}$

(b) Assume all the bromine in the flask is vapor.

$$P_{\text{calc}} = \frac{(2.00 \text{ g}) \times (1 \text{ mol}/159.8 \text{ g}) \times (0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}) \times (298 \text{ K})}{2.00 \text{ L}} = 0.153 \text{ atm} = 116 \text{ mm Hg}$$

$\text{VP} > P_{\text{calc}}$ ; assumption is correct;  $P$  in the flask is  $116 \text{ mm Hg}$ . The flask contains only vapor.

(c) Assume all the bromine in the flask is vapor.

$$P_{\text{calc}} = \frac{(2.00 \text{ g}) \times (1 \text{ mol}/159.8 \text{ g}) \times (0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}) \times (298 \text{ K})}{0.750 \text{ L}} = 0.408 \text{ atm} = 310 \text{ mm Hg}$$

$\text{VP} < P_{\text{calc}}$ ; assumption is wrong;  $P$  in the flask is  $228 \text{ mm Hg}$ . The flask contains liquid and vapor.

7. (a)  $\ln \frac{448}{197} = \frac{\Delta H}{8.31} \left[ \frac{1}{296} - \frac{1}{318} \right]; \quad \Delta H = 2.92 \times 10^4 \text{ J} = 29.2 \text{ kJ}$

(b)  $\ln \frac{760}{197} = \frac{29200}{8.31} \left[ \frac{1}{296} - \frac{1}{T} \right]; \quad T = 334 \text{ K} = 61^\circ\text{C}$

9.  $\ln \frac{760}{P} = \frac{40700}{8.31} \left[ \frac{1}{350} - \frac{1}{373} \right]; \quad P = 321 \text{ mm Hg}$

11. (a)  $\ln \frac{(1.75)(760)}{625} = \frac{40700}{8.31} \left[ \frac{1}{367.6} - \frac{1}{T} \right]; \quad T = 390 \text{ K} = 117^\circ\text{C}$

(b)  $117^\circ\text{C} - 94.5^\circ\text{C} = 23^\circ\text{C}$

13. The graph is linear;  $\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{-\Delta H_{\text{vap}}}{R}$

Use any two points on the  $y$ -axis and the corresponding  $x$ -axis:

$$\frac{-\Delta H_{\text{vap}}}{R} = \frac{\ln 400 - \ln 10}{(1/377) - (1/299.2)} \quad \text{where } R = 8.31 \text{ J/mol} \cdot \text{K}; \quad \Delta H_{\text{vap}} = 39.8 \text{ kJ}$$

15. (a) solid (b) liquid (c) vapor

17. (a) A (b) supercritical fluid (c) no (d) F  
(e) yes (f) no (g) no

19. (a) sublimes (b) melts (c) liquifies (d) liquifies

21. (a) Phase diagram similar to Figure 9.7 (a) with the triple point at 281 mm Hg on the  $y$  - axis and  $-121^\circ\text{C}$  on the  $x$  - axis. A point on the vapor-liquid equilibrium curve should have 760 mm Hg on the  $y$  - axis and  $-108^\circ\text{C}$  on the  $x$  - axis.

(b)  $\approx 500 \text{ mm Hg}$  (c) yes

23. (a) Phase diagram similar to Figure 9.7 (a) with the triple point at 20 mm Hg on the  $y$  - axis and  $90^\circ\text{C}$  on the  $x$  - axis. A point on the vapor-liquid equilibrium curve should have 760 mm Hg on the  $y$  - axis and  $120^\circ\text{C}$  on the  $x$  - axis.

(b)  $\approx 120^\circ\text{C}$  (c) liquid vaporizes

25. (a)  $> (d) > (c) > (b)$

27. All show dispersion forces; (c) and (d) show dipole forces.

29. (a), (c), (d)

31. (a) stronger dispersion forces

(b) stronger dispersion forces

(c) hydrogen bonding

(d) ionic vs molecular

33. (b), (d)

35. (a)  $\text{PCl}_3$ ; molecular vs ionic

(b)  $\text{AsH}_3$ ; no H bonds

(c)  $\text{C}_2\text{H}_5\text{OCH}_3$ ; no H bonds

(d)  $\text{HCl}$ ; weaker dispersion forces

37. (a) dispersion forces

(b) ionic bonds

(c) dispersion forces

(d) dispersion forces

39. (a) network covalent

(b) molecular

(c) ionic

41. (a) molecular

(b) metallic

(c) molecular

43. (a) metallic

(b) ionic

(c) molecular

(d) molecular

(e) ionic

45. (a)  $\text{C}_{60}$ ,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

(b)  $\text{Na}_2\text{CO}_3$

(c) graphite

(d) steel

47. (a)  $\text{Na}^+$ ,  $\text{I}^-$  ions

(b)  $\text{N}_2$  molecules

(c)  $\text{K}^+$ ,  $\text{O}^{2-}$  ions

(d)  $\text{Au}^+$  ions,  $e^-$

49.  $s^3 = 0.0375 \text{ nm}^3$ ;  $s = 0.335 \text{ nm}$ ;  $\frac{r}{s} = \frac{0.145}{0.335} = 0.433 = \frac{\sqrt{3}}{4}$ ; body-centered cubic

51.  $s = \frac{4r}{\sqrt{2}} = \frac{4(0.181 \text{ nm})}{1.414} = 0.512 \text{ nm}$

53. (a)  $0.513 \text{ nm} - 0.362 \text{ nm} = 0.151 \text{ nm}$

(b) no: ( $2r = 0.190 \text{ nm}$ ); no: ( $2r = 0.266 \text{ nm}$ )

55.  $s\sqrt{3} = 2(r \text{ Cs}^+ + r \text{ Cl}^-)$

57. (a) 4

(b) 8 for 4  $\text{Cl}^-$  at the corners; 2 for  $\text{Cl}^-$  in center

59. % humidity =  $P_{\text{H}_2\text{O}}/P_{\text{TOT}}$ ;  $P_{\text{H}_2\text{O}} = (0.38)(26.74) = 10.17 \text{ mm Hg}$

$$\text{mol water vapor at } 27^\circ\text{C} = \frac{(10.17/760 \text{ atm})(1.25 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(300 \text{ K})} = 6.79 \times 10^{-4} \text{ mol}$$

$$\text{mol water vapor at } 5^\circ\text{C} = \frac{(6.54/760 \text{ atm})(1.25 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(278 \text{ K})} = 4.71 \times 10^{-4} \text{ mol}$$

$$\text{mol water condensed} = (6.79 \times 10^{-4}) - (4.71 \times 10^{-4}) = 2.08 \times 10^{-4} \text{ mol}$$

$$\text{mass water condensed} = (2.08 \times 10^{-4} \text{ mol})(18.02 \text{ g/mol}) = 0.00374 \text{ g}$$

61. (a) water vapor pressure before compression = water vapor pressure after compression = 23.76 mm Hg

The pressure can only change if the volume is increased.

$$\text{(b) moles of water before compression} = \frac{(23.76/760 \text{ atm})(5.25 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.00671 \text{ mol}$$

$$\text{moles of water after compression} = \frac{(23.76/760 \text{ atm})(2.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.00256 \text{ mol}$$

$$\text{mass of water condensed} = (0.00671 \text{ mol} - 0.00256 \text{ mol})(18.02 \text{ g/mol}) = 0.0749 \text{ g}$$

63.  $V = (15 \times 12 \times 8.0) \text{ ft}^3 \times \frac{28.32 \text{ L}}{1 \text{ ft}^3} = 4.1 \times 10^4 \text{ L}$

$$n = \frac{(1.63 \times 10^{-3}/760 \text{ atm})(4.1 \times 10^4 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 3.6 \times 10^{-3} \text{ mol}$$

$$\text{Volume of Hg(l)} = 3.6 \times 10^{-3} \text{ mol} \times \frac{200.6 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mL}}{13 \text{ g}} = 5.5 \times 10^{-2} \text{ mL}$$

65.  $\ln \frac{760 \text{ mm Hg}}{37.0 \text{ mm Hg}} = \frac{\Delta H_{\text{vap}}}{0.00831 \text{ kJ/mol} \cdot \text{K}} \left( \frac{1}{293 \text{ K}} - \frac{1}{360 \text{ K}} \right)$ ;  $\Delta H_{\text{vap}} = 39.5 \text{ kJ}$

$$\ln \frac{P_2}{37.0 \text{ mm Hg}} = \frac{39.5 \text{ kJ}}{0.00831 \text{ kJ/mol} \cdot \text{K}} \left( \frac{1}{293 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$
;  $P_2 = 48.6 \text{ mm Hg}$

$$\text{moles of CH}_3\text{N}_2\text{H}_3 \text{ in } 1 \text{ L} = \frac{(48.6/760 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.00261 \text{ mol}$$

$$\text{mass of CH}_3\text{N}_2\text{H}_3 \text{ in } 1 \text{ L} = (0.00261 \text{ mol/L})(46.08 \text{ g/mol}) = 0.120 \text{ g/L}$$

67. (a) Ten water molecules at the bottom of the container.

(b) Ten water molecules spread out evenly through the container.

(c) Ten hydrogen molecules (small) and five oxygen molecules (larger)

69. (a) EQ (b) MI (depends on the amount of ether in the flask)

(c) GT (d) LT (e) GT

71. (a) strongly dependent on  $T$  (b) not true; dipole forces, hydrogen bonds

(c) true (d) only at critical  $P$  or below

73. A = iodine, B = iron sulfide, C = silver, D = graphite

$$75. \ln \frac{760 \text{ mm Hg}}{110 \text{ mm Hg}} = \frac{\Delta H_{\text{vap}}}{0.00831 \text{ kJ/mol} \cdot \text{K}} \left( \frac{1}{298 \text{ K}} - \frac{1}{350 \text{ K}} \right); \quad \Delta H_{\text{vap}} = 32.2 \text{ kJ/mol}$$

$$20.0 \text{ L} \times (1000 \text{ mL/L}) \times (1.59 \text{ g/mL}) \times (1 \text{ mol}/153.8 \text{ g}) = 206.8 \text{ mol}$$

$$\text{heat required} = (206.8 \text{ mol})(32.2 \text{ kJ/mol}) = 6.66 \times 10^3 \text{ kJ}$$

$$76. V_{\text{molar}} = \frac{55.85 \text{ g}}{7.86 \text{ g/cm}^3} = 7.11 \text{ cm}^3$$

$$0.496 \text{ nm} = s \sqrt{3}; \quad s = 0.286 \text{ nm}; \quad V_{\text{atom}} = \frac{(0.286 \text{ nm})^3}{2} = 1.17 \times 10^{-2} \text{ nm}^3 = 1.17 \times 10^{-23} \text{ cm}^3$$

$$N_{\text{A}} = \frac{7.11}{1.17 \times 10^{-23}} = 6.08 \times 10^{23}$$

77. (a) 3.60 g water formed

$$\text{mass of H}_2\text{O}(g) = \frac{(18.02 \text{ g/mol})(26.74/760 \text{ atm})(10.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(300 \text{ K})} = 0.257 \text{ g}; \quad \text{liquid and vapor}$$

(b) 26.7 mm Hg

$$(c) 2.80 \text{ g H}_2 \text{ remains}; \quad P_{\text{H}_2} = \frac{(2.80/2.016 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(300 \text{ K})}{10.0 \text{ L}} = 3.42 \text{ atm}$$

$$P_{\text{Tot}} = 3.42 \text{ atm} + 0.04 \text{ atm} = 3.46 \text{ atm}$$

$$78. \ln \frac{760 \text{ mm Hg}}{100.0 \text{ mm Hg}} = \frac{\Delta H}{8.31 \text{ J}} \left( \frac{1}{293.2 \text{ K}} - \frac{1}{347.3 \text{ K}} \right); \quad \Delta H = 31.7 \text{ kJ/mol}$$

$$39^\circ\text{F} = 4^\circ\text{C} = 277 \text{ K}$$

$$\ln \frac{100.0 \text{ mm Hg}}{P} = \frac{31700}{8.31 \text{ J}} \left( \frac{1}{277 \text{ K}} - \frac{1}{293 \text{ K}} \right); \quad P = 47 \text{ mm Hg}$$

$$\text{mass of vapor} = \frac{(133.4 \text{ g/mol})(47/760 \text{ atm})(18 \times 28.32 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(277 \text{ K})} = 1.8 \times 10^2 \text{ g}$$

$$\text{original mass} = 0.500 \text{ pt} \times \frac{1 \text{ qt}}{2 \text{ pt}} \times \frac{1 \text{ L}}{1.057 \text{ qt}} \times \frac{10^3 \text{ cm}^3}{1 \text{ L}} \times \frac{1.325 \text{ g}}{1 \text{ cm}^3} = 313 \text{ g}$$

$$\% \text{ left} = \frac{133}{313} \times 100\% = 42\%$$

$$79. \frac{120 \text{ lb}}{0.10 \text{ in}^2} \times \frac{1 \text{ atm}}{15 \text{ lb/in}^2} = 80 \text{ atm}$$

$80/134 = 0.60^\circ\text{C}$ ; but heat conduction is more likely, but see *Scientific American*, Feb. 2000, p. 50

$$80. 4r_{\text{anion}} = \sqrt{2}(2r_{\text{anion}} + 2r_{\text{cation}}) \quad \frac{2r_{\text{cation}}}{2r_{\text{anion}}} = \frac{4 - 2\sqrt{2}}{2\sqrt{2}} = \frac{4 - 2.828}{2.828} = 0.4144$$

81.  $P_{\text{C}_3\text{H}_8}$  is the vapor pressure of propane, which decreases exponentially with  $T$ ;  $P_{\text{N}_2}$  is the gas pressure, which decreases linearly with  $T$ .